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(54) Title: FINELY DIVIDED METAL CATALYST AND METHOD FOR MAKING SAME

(57) Abstract: An inexpensive, highly catalytic material preferably formed by a leaching process. The catalyst comprises a finely divided metal particulate and a support. The active material may be a nickel and/or nickel alloy particulate having a particle size less than about 100 Angstroms. The support may be one or more metal oxides.

FINELY DIVIDED METAL CATALYST AND METHOD FOR MAKING SAME**RELATED APPLICATION INFORMATION**

5 This application is a continuation-in-part of commonly assigned U.S. Patent Application Serial Number 09/290,633.

FIELD OF THE INVENTION

10 The present invention relates generally to inexpensive catalytic material and more specifically to non-platinum and non-palladium catalytic materials as well as to inexpensive methods for manufacturing same.

BACKGROUND OF THE INVENTION

15 A fuel cell is an electrochemical device in which the chemical energy of a conventional fuel is converted directly and efficiently into low voltage electrical energy. Fuel cells have many potential applications such as supplying power for transportation vehicles, replacing steam turbines and remote power supply applications.

20 Fuel cells, like conventional batteries, operate by utilizing electrochemical reactions. Unlike a battery, in which chemical energy is stored within the cell, fuel cells generally are supplied with reactants from outside the cell. Barring failure of the electrodes, as long as the fuel
25 (preferably hydrogen), and the oxidant (preferably either oxygen or air that contains oxygen), are supplied and the reaction products are removed, the cell continues to operate.

Fuel cells also offer a number of important advantages over engine or generator systems. They include relatively
30 highly efficient, environmentally clean operation especially when utilizing hydrogen as a fuel, high reliability, few moving parts, and quiet operation.

A schematic diagram of a fuel cell with the reactant/product gases and the ion conduction flow directions
35 through the cell is shown in Figure 4. Referring to Figure 4, the major components of a typical fuel cell 10 is an anode 14,

a cathode 16 and an electrolyte layer 12. In the embodiment shown, the anode 14 and the cathode 16 are each in contact with and positioned on opposite sides of the electrolyte layer. During operation, a continuous flow of fuel, commonly hydrogen, is fed to the anode 14 while, simultaneously, a continuous flow of oxidant, commonly oxygen or air, is fed to the cathode 16. In the example shown, the hydrogen is fed to the anode 14 via a hydrogen compartment 13. Likewise, the oxygen or air is fed to the cathode 16 via an oxygen/air compartment 17. The fuel is oxidized at the anode with a release of electrons through the agency of a catalyst. These electrons are conducted from the anode 14 through wires external to the cell, through the load 18, to the cathode 16 where the oxidant is reduced and the electrons are consumed, again through the agency of a catalyst. The constant flow of electrons from the anode 14 to the cathode 16 constitutes an electrical current that can be made to do useful work. Typically, the reactants such as hydrogen and oxygen, are respectively fed through the porous anode 14 and cathode 16 and brought into surface contact with the electrolyte 12. The particular materials utilized for the anode 14 and cathode 16 are important since they must act as efficient catalysts for the reactions to take place.

Despite their potential advantages, fuel cells have not been widely utilized due in large part to their relatively high cost. An important factor contributing to this high cost is the catalytic inefficiencies of the prior art catalytic materials and/or the high costs of many of these materials. The catalytic inefficiencies of the materials increase the operating costs of the fuel cell since such inefficiencies result in a lower electrical energy output for a given amount of fuel. The use of expensive catalytic materials, such as noble metal catalysts, results in fuel cells which are too

expensive for widespread application.

High catalytic efficiency at low cost is a desired result which must be attained before widespread commercial utilization of fuel cells is possible. Prior art fuel cell anode catalysts, which have been generally predicated on either expensive noble metal catalysts with a relatively low density of catalytically active sites, have not been able to meet the requirements. The present invention is directed toward novel, low cost and highly efficient catalytic materials that are useful for a variety of applications such as a fuel cell anode. The present invention is also directed toward an efficient and inexpensive method of making the novel catalytic materials.

SUMMARY OF THE INVENTION

An objective of the present invention is an inexpensive, highly catalytic material that may be used for facilitating hydrogen consumption in a fuel cell anode. Another objective of the present invention is a catalytic material having a finely divided metal particulate with very small particle size. Yet another objective of the present invention is a cost effect method for making the instant catalytic materials. Yet another objective of the present invention is a fuel cell anode and a fuel cell incorporating the instant catalytic materials.

These and other objectives are satisfied by a catalyst lacking platinum and palladium, the catalyst comprising: a metal particulate having a particle size less than about 100 Angstroms; and a support.

These and other objectives are also satisfied by a catalyst, comprising: a nickel and/or nickel alloy particulate having a particle size less than about 100 Angstroms, the nickel alloy lacking platinum and palladium; and a support.

These and other objectives are also satisfied by a catalyst comprising a metal particulate and a support, the catalyst characterized by being formed by the process comprising the step of leaching at least a significant portion of the bulk of a hydrogen storage alloy.

These and other objectives are satisfied by a method for making a catalyst, comprising the steps of: providing a hydrogen storage alloy; and leaching at least a significant portion of the bulk of the alloy.

These and other objectives are satisfied by a fuel cell, comprising: an anode having a catalyst lacking platinum and palladium, the catalyst comprising: a metal particulate having a particle size less than about 100 Angstroms, and a support. The fuel cell preferably further comprise a cathode and an electrolyte. The electrolyte may comprise an alkaline material.

These and other objectives are satisfied by a fuel cell, comprising: an anode having a catalyst comprising: a nickel and/or nickel alloy particulate having a particle size less than about 100 Angstroms, the nickel alloy lacking platinum and palladium, and a support. The fuel cell preferably further comprises a cathode and an electrolyte. The electrolyte may comprise an alkaline material.

25

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is an STEM photomicrograph showing the effects of leaching a hydrogen storage alloy particle with an alkaline solution;

Figure 2 is an STEM photomicrograph of the instant catalytic material, performed under Brightfield imaging, showing the catalytically active nickel rich regions;

Figure 3 is an STEM photomicrograph, performed under

Darkfield imaging, of the same region of catalytic material from Figure 2;

Figure 4 is a schematic diagram of a fuel cell;

5 Figure 5 is a diagram of an alkaline fuel cell using the catalyst of the present invention;

Figure 6 is a diagram showing an example of an anode layer for an alkaline fuel cell comprising a catalyst and a hydrophobic material;

10 Figure 7 is a diagram showing cell voltage and pressure versus time for a Ni-MH cell charged at C/10 rate for twenty hours;

Figure 8 is a diagram showing cell voltage and pressure versus time for the Ni-MH cell of Figure 7, with the cell kept idle in the open configuration for five hours;

15 Figure 9 is a diagram showing cell voltage and pressure versus time for a Ni-MH cell charged and discharge after multicycling and then charged at C/10 rate for twenty hours; and

20 Figure 10 is a diagram showing cell voltage and pressure versus time for the Ni-MH cell of Figure 9, with the cell kept in open circuit in the open configuration for five hours.

DETAILED DESCRIPTION OF THE INVENTION

25 Disclosed herein is a novel catalyst particularly useful for facilitating the consumption of molecular hydrogen in a fuel cell anode. The catalyst is designed to have a high density of catalytically active sites to provide efficient, low cost fuel cell operation. With a greater density of
30 catalytically active sites, the hydrogen oxidation reaction occurs much more readily to allow for more efficient hydrogen consumption at reduced costs.

Generally, the catalyst of the present invention

comprises a metal particulate, and a support. The particulate may be affixed to the surface of the support. Alternately, the particulate may be partially or totally embedded into the support. The metal particulate is a plurality of metal particles. Preferably, each metal particle may be a substantially pure elemental metal, or it may be an alloy of two or more elemental metals. It is also possible that one or more of the individual particles may be a composite or mixture of two or more elemental metals, two or more alloys, or an elemental metal and an alloy. All of the particles may have the same composition or they may be a mixture of particles with different compositions. Also, some of the particles may be substantially pure elemental metals while others may be alloys of two or more elemental metals

In one preferred embodiment of the present invention, the catalyst lacks both platinum and palladium. Hence, there are no platinum particles or palladium particles. As well, none of the metal particles comprise either platinum or palladium as part of an alloy, composite or mixture.

In another embodiment of the present invention, the metal particulate comprises nickel particles and/or nickel alloy particles. The nickel alloy includes nickel and at least one additional elemental metal. Preferably, the at least one additional elemental metal may be any elemental metal except for either platinum or palladium. (Hence, it is preferable that the nickel alloy lacks both platinum and palladium). More preferably, the at least one additional elemental metal is selected from the group consisting of Al, Co, Sn, Mn, Ti and Fe. Most preferably, the at least one additional elemental metal is selected from the group consisting of Al, Co, Sn, Mn, and Ti. Examples of nickel alloys which may be used include nickel alloys comprising Ni and Co; nickel alloys comprising Ni, Co and Al; nickel alloys comprising Ni, Co, Mn and Ti;

nickel alloys comprising Ni, Co, Mn and Fe; and nickel alloys comprising Ni and Mn. Specific examples of nickel alloys include a NiCo alloy, a NiCoAl alloy, a NiCoMnTi alloy, a NiCoMnFe alloy, and a NiMn alloy.

5 It is believed that the addition of modifier elements to the nickel to form a nickel alloy increases the surface roughness of the metal particles. Since surface roughness is the total surface area divided by the geometric surface area, the increased roughness provides for an increase in the total
10 surface area of the metal particulate. The increased surface area provides for an increase in the number of active catalysis sites (i.e., there is increased accessibility to the catalytic material). Hence, the catalytic activity of the material is increased.

15 The increased surface area also makes the catalytic material less easy to poison. This is a crucial factor in the commercial viability of fuel cell anodes. Generally, poisoning is reduced as the number of active catalysis sites increases. As just discussed, this occurs with increased
20 surface roughness and surface area. (It is noted that surface area can also be increased in other ways besides increasing surface roughness. For example, surface area may be increased by making the metal catalytic particles smaller and packing them closer together. This will also decrease the
25 chance of the poisoning).

 The addition of modifier elements to the metallic nickel can also inhibit poisoning in other ways. Poisoning can be affected by the actual composition of the metallic particulate. By identifying the poison and the mechanism for
30 poisoning, a suitable modifier may be added to the metal particulate to combat the poisoning. For example, poisoning may be due to the build-up of a passivating oxide on the surface of the metal particulate, thereby impeding the H₂

dissociation reaction. In this case, a modifier element such as cobalt or aluminum could be added at a concentration which is effective to provide an ongoing leaching of the particulate by the electrolyte in order to constantly provide a clean, new metallic surface which is free of the passivating oxide.

Also, poisoning may be due to the corrosion of the particulate and/or its support by the electrolyte. In this case a passivating agent, such as Zr or Mn, could be added. Though not wishing to be bound by theory, it is possible that these modified catalysts may be especially resistant to H_2 contaminants such as H_2S , CH_4 , CO_2 , CO , which are aggressive poisons to fuel cell anode catalysts.

It is also believed that adding certain elements, such as Al, Sn and Co, to the nickel to form the nickel alloy may actually inhibit the growth of the alloy particles and cause the average size of the particles to remain small. As discussed above, decreasing the particle size while packing the particles closer together increases the total surface area of the particulate, increasing catalytic activity and decreasing the possibility of poisoning.

The catalytic metal particles of the present invention are not limited to any particular shape. They may be regularly shaped or irregularly shaped. Examples of particle shapes include spherical, elongated, thread-like, and "sponge-like". "Sponge-like", porous particles may be made by initially including in the metal particulate a modifier element, such as aluminum, whose sole purpose is to be leached out so as to leave the catalyst particulate with a sponge-like shape and a high surface area. The leaching step may be carried out by subjecting the alloy to an aqueous solution of an alkali metal hydroxide such as potassium hydroxide, lithium hydroxide, sodium hydroxide, or mixtures thereof. Preferably, the leaching may be done in a highly concentrated KOH solution

(perhaps about 45 wt% to about 60 wt%), at elevated temperature of about 80°C to about 120°C, for a time of about one hour to about four hours. Of course, other leaching conditions are also possible. After the leaching step, the remaining insoluble component forms a particulate with a sponge-like, porous structure. The increased porosity increases the surface area of the particulate.

It is noted that the catalytic activity of a material may be determined by measuring the material's exchange current I_0 (measured in mA/g). The exchange current I_0 is a function of both the material's exchange current density i_0 (measured in mA/m²) as well as the material's surface area A (m²/g). Specifically, the exchange current, the exchange current density and the surface area are all related as follows:

$$I_0 = i_0 \times A \quad (1)$$

Equation (1) shows that the total catalytic activity of a material (as measured by the total exchange current I_0) is a function of both the catalytic activity of the material composition (as measured by the exchange current density i_0) as well as the surface area of the material A . Hence, the total catalytic activity of a material may be increased by either appropriately changing its composition to one which is more catalytic or by increasing its effective surface area. As discussed above, the effective surface area may be increased by increasing the porosity and/or roughness of the catalytic particles. It also may be increased by using a larger number of smaller-sized particles, and by packing these smaller-sized particles closer together. The effective surface area may also be increased by increasing the porosity and surface area of the support upon which active material is dispersed. The support will be discussed in more detail

below.

Preferably, the catalytic metal particles of the present invention have a very small particle size. Specifically, the particles have an average particle size which is preferably less than about 100 Angstroms, more preferably less than about 70 Angstroms, and most preferably less than about 50 Angstroms. In addition, the particles may have an average particle size which is preferably be less than about 40 Angstroms and more preferably may have an average particle size which is less than about 30 Angstroms. In addition, the particulate may have a particle size between about 10 to about 70 Angstroms, preferably between about 10 to about 50 Angstroms, more preferably between about 10 to about 40 Angstroms and most preferably between about 10 and about 30 Angstroms.

A key aspect of the instant invention is the disclosure of a practical embodiment and method of producing "ultra fine catalysts". Since the catalytic properties of a material are primarily a surface property (rather than a bulk property), large catalytic metal particles essentially waste the interior metallic atoms. For expensive elements, such as platinum and palladium (well known to have the required stability for fuel cell anode use), this waste of material provides an unacceptable cost. Therefore, the smaller the metallic particles, the better since the surface area for catalysis rises proportionally. It is extremely difficult to produce Angstrom size metallic particles. Hence, the disclosure of 10-50 Angstrom size particles (which themselves may have additional surface area due to surface roughness) in a finely divided distribution within an inexpensive support is unique.

In certain embodiments of the present invention, the metal particles of the present invention are situated in close proximity to one another so that the particulate has a high

density. (Hence, there is also a high density of catalytic activity). The particulate may have an average proximity that is preferably between about 2 and about 300 Angstroms, and more preferably between about 50 to about 100 Angstroms.

5 In other embodiments of the invention the percentage weight of the metal may be varied so that the metal particulate is preferably between about .0001% to about 99% by weight of the catalyst, more preferably between about .001% to about 99% by weight of the catalyst, most preferably between about .01% to about 99% by weight of the catalyst.

10 Experimental observations from high resolution scanning transmission electron microscopy (STEM) of specific embodiments of the instant catalytic material show the presence of catalytic regions or "catalytic clouds". These
15 catalytic regions may comprise nickel and/or nickel alloy regions. The nickel or nickel alloy regions may be regions of metallic nickel particles and/or nickel alloy particles having an average size of about 10 to about 30 Angstroms in diameter. In some of these regions, the proximity between the particles
20 may be between about 10 to about 50 Angstroms. In other regions, the metallic nickel and/or nickel alloy particles are even more closely packed, having a proximity on the order of about 10 to about 20 Angstroms. Specifically, Figure 2 is an STEM photomicrograph of the instant catalytic material,
25 performed under Brightfield imaging, showing the catalytically active nickel rich regions. Figure 3 is an STEM photomicrograph, performed under Darkfield imaging, of the same region of catalytic material from Figure 2. Figure 3 shows the metallic nickel particles.

30 Preferably, the metal particulate of the present invention is "stable" over time. That is, preferably, the size of the particles remains small and does not increase over time. This helps to ensure that the total surface area of the

particulate remains stable (i.e., does not decrease) over time.

5 The catalyst of the present invention further comprises a support for the metal particulate. Generally, any support conventionally known in the art, capable of supporting and providing adequate dispersion for the particulate, may be used. Preferably, the support should be inexpensive and stable in the local environment in which it is being used. The
10 support used preferably has a surface area and/or porosity sufficient to provide an adequate dispersion of the metal particles, thereby allowing both penetration of electrolyte for the anode reaction, but preferably not allowing the electrolyte to penetrate to the H₂ gas compartment.

15 Increasing the porosity of the support also provides for a more intimate contact between the hydrogen gas reactant and the catalytic material. In the case of a liquid electrolyte, it also enhances the contact between the electrolyte and the catalytic particles thereby improving or optimizing proton
20 transfer. Generally, the metal particulate may be affixed to the surface of a support and/or partially embedded in the support and/or totally imbedded in the support.

25 The instant invention also facilitates introduction of an electrolyte impermeable membrane in combination with a current collection substrate such as wire mesh or expanded metal.

30 In one embodiment of the present invention, the support comprises one or more inorganic oxides. The inorganic oxides may be metal oxides. The oxides may comprise at least one element selected from the group consisting of nickel, cobalt, manganese, titanium, zirconium, iron and the rare earth elements. The oxides may comprise one or more individual oxides of the elements nickel, cobalt, manganese, titanium, zirconium, iron and the rare earth elements. Alternately, the

oxides may comprise one or more oxides of alloys formed from two or more of the elements nickel, cobalt, manganese, titanium, zirconium, iron and the rare earth elements.

5 In a first example, the support comprises an oxide of manganese. In a second example, the support comprises an oxide of nickel and manganese. In a third example, the support comprises an oxide of nickel, manganese, cobalt, and titanium. In a fourth example, the support comprises an oxide of nickel, manganese, cobalt, titanium and iron. In a fifth
10 example, the support comprises an oxide of nickel, manganese, cobalt and titanium. In a sixth example, the support comprises an oxide of titanium and zirconium. In a seventh example the support comprises silica. In an eighth example, the support comprises alumina. The metal particulate may be
15 affixed to the surface of the oxide support. Alternately, the metal particulate may be at least partially embedded within the oxide support, or it may be totally embedded within the oxide support.

20 In still another preferred embodiment of the instant invention, these ultra-fine catalysts may be combined with zeolite materials. The zeolites may have variable metal to silicon ratios, and the ratio of the catalyst to zeolite may also vary. A combination of catalyst/support oxide/zeolite is a preferred embodiment.

25 The oxide support may itself be catalytic. In fact, by using certain oxides as the support material, regions of exceptionally high catalytic activity may be formed, especially at the double or triple or more junctions between the metallic particle and the support oxide where designed
30 regions of hydrophobic or hydrophilic property may be formed. Analytical studies show that these regions are rich in such elements as nickel, cobalt, manganese and titanium, and are referred to herein as "NiCoMnTi super catalytic regions". It

is believed that these super catalytic regions may consist of nickel-manganese alloy particles embedded in a titanium-zirconium oxide. These super catalytic regions show a surprising lack of oxygen (based on the results of Electron Energy Loss Spectroscopy-EELS). It is also believed that the oxide portion of these regions may be partially metallic and/or exist in a low oxidation state.

The oxide support also may be formed from metal oxides which are "microcrystalline" in structure, having crystallites of very small size. Because of their small crystallite size, these oxides have an increased number of grain boundaries which provide "ionic pathways" for both hydrogen and hydroxyl ions. (These ionic pathways may permit the hydrogen and hydroxyl ions to move more freely to the metallic nickel or nickel alloy catalytic sites which may be situated in the grain boundaries). Hence, such oxides facilitate ionic transport through the catalytic material.

Alternately, the oxide support may be formed so that it at least partially comprises a "multivalent" oxide material such as manganese oxide, MnO_x . Because manganese oxide is multivalent, it is believed that it may further promote increased catalytic activity by changing oxidation states.

It is also possible to add a polymeric material to the oxide support in order to modify the hydrophobic/hydrophilic nature of the catalyst bed. Examples of such polymers include fluoropolymers such as polytetrafluoroethylene (PTFE).

The oxide support may comprise fine-grained oxides, coarse-grained oxides or a mixture of fine-grained oxides and coarse-grained oxides. Alternately, the oxide support may be formed so that it comprises a "multi-phase" oxide material. For example, the oxide may be formed so that it includes both fine-grained and coarse-grained regions. The fine-grained region may include oxides such as a manganese oxide MnO_x , a

NiMnCoTi oxide or a MnCoTi oxide. One advantage of a multiphase oxide may be the suitable structural integrity of the fuel cell anode to withstand the rigors of transportation where vibration can cause premature fuel cell failure. The
5 coarse-grained regions may include oxides such as a TiZr oxide.

The catalytic materials of the present invention may be formed so that the metal particles have certain crystal structures (based on Select Area Electron Diffraction - SAED)
10 within the oxide support. For example, catalytic materials comprising nickel alloy particles embedded within an oxide material may be formed so that the alloy particles have a face-center-cubic (fcc) structure. The formation of an fcc crystal structure may be influenced by the high degree of
15 substitution of the modifier elements (such as Co, Al, Mn, Sn) for the nickel. The fcc nickel alloy in conjunction with the NiCoMnTi super catalytic regions and the TiZr oxide forms a structure which may further promote ionic diffusion and reaction. In an alternate embodiment of the present
20 invention, the support may be formed from a carbon material. Examples of carbon supports include carbon black, graphite, activated carbon, charcoal and carbide. Mixtures of carbon materials and inorganic oxides may also be used. Alternately, the support may comprise a carbide. For example, the support
25 may comprise a binary compound of carbon and another element. (Examples of carbides include those of calcium, tungsten, silicon, boron, and iron). Additionally, other mixtures or blends of supports can be used to provide high surface area for the catalytic metal particulate and good electronic
30 conductivity as well as good ionic transport.

Alternately, the support may comprise a halide such as a chloride. Alternately, the support may comprise a phosphide, a silicide, or a nitride. Of course, the support may be a

blend or mixture of the materials described above.

One of the starting materials for the formation of the catalytic materials of the present invention are hydrogen storage alloys. These are materials which are capable of the absorption and release of hydrogen. Hydrogen storage alloys are known in the art. Examples of very simple hydrogen storage alloys are the TiNi and LaNi₅ alloys. Other examples of hydrogen storage alloys are provided in U.S. Patent No. 4,623,597 (the disclosure of which is incorporated by reference). The materials described in the '597 Patent have a greatly increased density of catalytically active sites providing for the fast and stable storage and release of hydrogen. These materials were fabricated by manipulating the local chemical and structural order by incorporating selected modifier elements into a host matrix so as to create the desired disorder. Additional hydrogen storage alloys are disclosed in U.S. Patent No. 4,551,400 ("the '400 Patent"), the disclosure of which is incorporated by reference. These materials utilize a generic Ti-V-Ni composition where at least Ti, V, and Ni are present with at least one or more of Cr, Zr, and Al. Other Ti-Vi-Zr-Ni alloys are described in U.S. Patent No. 4,728,586 ("the '586 Patent"), the disclosure of which is incorporated by reference. The '586 Patent described a specific sub-class of these Ti-V-Ni-Zr alloys comprising Ti, V, Zr, Ni, and a fifth component Cr. Modified LaNi₅ materials are discussed in U.S. Patent No. 5,096,667, ("the '667 Patent") the contents of which is incorporated by reference herein. Still other examples of hydrogen storage alloys are described in U.S. Patent Nos. 5,840,440, 5,536,591 ("the '591 Patent") and in commonly assigned U.S. Patent Application 09/290,633 ("the '633 Application"). The contents of U.S. Patents Nos. 5,840,440, and 5,536,591 as well as the contents

of U.S. Patent Application 09/290,633 are all incorporated by reference herein.

Examples of alloys described in the '591 Patent are alloys having the composition:

5 (Base Alloy)_aCo_bMn_cFe_dSn_e

where Base Alloy comprises 0.1 to 60 atomic percent Ti, 0.1 to 40 atomic percent Zr, 0 to 60 atomic percent V, 0.1 to 57 atomic percent Ni, and 0 to 56 atomic percent Cr; b is 0 to 7.5 atomic percent; c is 13 to 7 atomic percent; d is 0 to 3.5 atomic percent; e is 0 to 1.5 atomic percent; and a+b+c+d+e=100 atomic percent. Many of the alloys described in the '591 Patent include Mn, the effects of which is discussed in the '667 Patent, the disclosure of which is incorporated by reference herein.

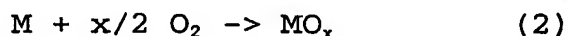
15 The '633 Application describes certain hydrogen absorbing alloys formed by adding one or more modifier elements to certain "base" alloys. The base alloys preferably have a composition consisting essentially of 0.1 to 60% Ti, 0.1 to 40% Zr, 0 to 60% V, 0.1 to 57% Ni, 5 to 22% Mn and 0 to 56% Cr. The modified alloys which are described in the '633 Application are referred to herein as "the '633 alloys".

20 Preferably, the modifying elements are chosen from the group consisting of Al, Co, Sn, and Fe. More preferably, the modifying elements are chosen from the group consisting of Al, Co, and Sn. In a first example, all three modifying elements, Al, Co, and Sn are added to the base alloy. In a second example, all four modifying elements, Al, Co, Sn and Fe are added to the base alloy. In a third example, the modifier elements may added to the base alloy so that the atomic percentage of Al is between about 0.1 and about 10, the atomic percentage of the Co is between about 0.1 and about 10, the atomic percentage of the Sn is between about 0.1 and about 3.0, and the atomic percentage of the Fe is between about 0.0

and about 3.5. In a fourth example, the modifier elements may be added to the base alloy so that the resulting modified alloy has the following composition:

$\text{Ti}_{9.0}\text{Zr}_{26.2}\text{V}_{5.0}\text{Vi}_{38.0}\text{Cr}_{3.5}\text{Co}_{1.5}\text{Mn}_{15.6}\text{Al}_{0.4}\text{Sn}_{0.8}$.

5 Hydrogen storage alloys tend to react with oxygen to form metal oxides by the reaction:



10 Hydrogen storage alloys are sensitive to the formation of surface oxides so that most, if not all, of these alloys comprise an initial surface oxide layer. The composition of this initial surface oxide layer depends, at least in part, on the composition of the underlying bulk alloy material (that
15 is, upon the constituent metals which make up the bulk material as well as the atomic percentage of those metals). The oxide surface layer is typically between about 50 Angstroms to about 1000 Angstroms thick, although thicknesses of the surface oxide layer of up to about 5000 Angstroms are
20 possible.

The initial surface oxide of a hydrogen storage alloy may be modified by an etch process. Alkaline etch processes are described in U.S. Patent No. 4,716,088 ("the '088 Patent") as well as in commonly assigned U.S. Patent Application
25 09/395,391 ("the '391 Application"). Both the '088 Patent as well as the '391 Application are incorporated by reference herein. As described in the '088 Patent, the major role of the etch process is that of surface modification. The '088 Patent, '391 Application as well as the '591 Patent and the
30 '633 Application describe the effects of the etch process on the surface oxide.

A method of making the catalytic material of the present invention is by subjecting a hydrogen storage alloy starting

material (which is preferably in the form of a powder) to a leaching process (also referred to herein as a "leaching treatment"). The leaching process of the present invention is a deep, penetrating "bulk" leaching process. This means that the leaching material (the active material that does the leaching - also referred to as "leaching agent" or "leachant") penetrates well below the 5000 Angstrom initial surface oxide layer of the alloy particle and into the particle bulk. As used herein, "bulk" refers to the interior region of the particle beneath the 5000 Angstrom oxide surface layer. The leaching process penetrates and treats (i.e., leaches) at least a significant portion of the bulk of the alloy particle. Preferably, a significant portion of the bulk is leached when the leaching process treats at least about 10,000 Angstroms of the hydrogen storage alloy particle. Hence, it is preferable that at least about a 10,000 Angstrom thick layer of the hydrogen storage alloy particle is leached. More preferably, at least about 20,000 Angstroms of the particle is leached. Most preferably, at least about 30,000 Angstroms of the particle is leached. In another embodiment of the method, it is preferable to leach at least about 40,000 Angstroms of the particle. It is more preferable to leach at least about 50,000 Angstroms of the particle. In a preferred embodiment of the method, it is preferable to leach substantially the entire bulk of the hydrogen storage alloy material. Hence, in a preferred embodiment, substantially the entire hydrogen storage alloy particle is leached.

In other embodiments of the instant invention preferably at least about 10% of the hydrogen storage alloy particle is leached, more preferably at least about 25% of the hydrogen storage alloy particle is leached, and most preferably at least about 50% of the hydrogen storage alloy particle is leached. In yet other embodiment of the instant invention

preferably at least about 75% of the hydrogen storage alloy particle is leached, and more preferably at least about 90% of the hydrogen storage alloy particle is leached.

5 As described above, an embodiment of the instant catalytic materials is a finely divided metal particulate embedded in an oxide support. In particular, the metal particulate may be a metallic nickel and/or a nickel alloy where the nickel alloy lacks both platinum and palladium. This embodiment may be made by subjecting the hydrogen storage
10 alloy material to the appropriate leaching process. The leaching process penetrates into substantially the entire particle bulk and converts the oxidizable components of substantially the entire bulk of the alloy particle to oxides. Hence, the oxidizable components of substantially the entire
15 alloy particle in converted to oxides.

The hydrogen storage alloy may be subjected to a leaching process by "contacting" the alloy material with an appropriate leaching material for a predetermined period of time, at a specific temperature and at a specific pH. To convert the
20 alloy material to oxide, the appropriate leaching material may be an alkaline solution. The hydrogen storage alloy may be "contacted" with the alkaline solution by placing the alloy (which is preferably in powder form) in a container of the alkaline solution. The alkaline solution is preferably formed
25 as an aqueous solution of an alkali metal hydroxide. Examples of alkali metal hydroxides which may be used include potassium hydroxide, sodium hydroxide, lithium hydroxide, and mixtures thereof. The pH of the alkaline solution may be adjusted by changing its alkaline concentration. The alkaline
30 concentration is adjusted by changing the percentage weight of the alkali metal hydroxide added to the aqueous solution. The period of time in which the leaching material (i.e., in this case, the alkaline solution) is in contact with the